

Environmental Cracking in Structural Alloys

Thomas W. Crooker

What Is It?

Environmental cracking encompasses two well-known failure phenomena, corrosion fatigue and stress-corrosion cracking. In simplest terms, corrosion fatigue refers to the interaction of environment and cyclic stress, and stress-corrosion cracking involves the interaction of environment and sustained tensile stress. The two phenomena may be related, especially at the basic mechanism level, but they also exhibit important differences which can be of engineering significance, especially at the phenomenological level. Both phenomena can exhibit two stages of failure: (i) crack initiation, where previously unflawed material slowly develops a crack due to the combined action of environment and stress and (ii) crack propagation, where the crack grows slowly due to the combined action of environment and stress. In stress-corrosion cracking, an intermediate stage referred to as incubation can also occur, where an existing crack remains dormant, prior to initiating growth, under stress while crack-tip reactions are occurring. If left unchecked, environmental cracking can lead to mechanical failure. Generally, the mechanical fracture process that subsequently occurs, be it of a brittle or ductile nature, is unaffected by the environmentally-assisted process that preceded it. Also, the two environmental cracking phenomena can interact synergistically.

Corrosion fatigue and stress-corrosion cracking have been recognized for many years as potentially dangerous failure mechanisms in structural alloys. One of the more dramatic examples of failure involving environmental cracking was the collapse of the Point Pleasant Bridge at Point Pleasant, West Virginia on December 15, 1967.¹ This bridge collapsed without warning as a result of environmental cracking which led to brittle fracture of a high-strength steel eyebar suspension member.

Because of its complexity and because of its importance to modern technological activities such as defense, transportation and energy, research into environmental cracking has been very active in recent years. So far in

the 1980's, frequent symposia on various aspects of the subject have been held in this country and abroad.²⁻⁵ It has also been the subject of a recent study by the National Materials Advisory Board.⁶

ASTM Committees E-09, E-24 and G-01 each conduct activities on various aspects of environmental cracking. This article will focus on the activities in Committee E-24 to develop ASTM standards on fracture mechanics test methods for corrosion fatigue and stress-corrosion cracking in precracked specimens in aqueous environments.

How Aqueous Environments Affect Cracking Behavior

Under cyclic stress, aqueous environments will generally accelerate fatigue crack growth. Under sustained tensile stress, the environment may cause spontaneous crack growth in certain susceptible alloys. Sensitivity to accelerated crack growth in corrosion fatigue is widespread among engineering alloys. Most commonly-used structural alloys can be affected in this way by corrosion fatigue. However, susceptibility to stress-corrosion cracking is more specific and tends to occur in high-strength alloys; although several very important exceptions to this generalization do occur, perhaps most notably among austenitic stainless steels widely used in nuclear pressure vessel and piping applications and among copper alloys in ammonia environments.

For high-strength alloys, susceptibility to stress-corrosion cracking is clearly a prime consideration which limits their structural usefulness in aggressive environments. Conversely, many of the widely-used conventional low- and intermediate-strength structural alloys do not appear to exhibit stress-corrosion cracking susceptibility in commonly encountered environments.

Fracture mechanics has been of great importance in developing test methods and engineering methodology for environmental cracking; although the fracture mechanics approaches to corrosion-fatigue crack growth and stress-corrosion cracking differ in some important ways. These similarities and differences can be seen by examining the fracture-mechanics-based methodology for experimentally characterizing corrosion-fatigue crack growth and stress-corrosion cracking, shown schematically in Figures 1 and 2.

Figure 1 illustrates the most commonly used basis for describing fatigue crack growth. Fatigue crack growth rates (i. e., the average crack

extension per cycle of repeated loading, da/dN) are plotted on log-log coordinates versus the crack-tip stress-intensity range (ΔK). In the absence of an aggressive environment, da/dN -versus- ΔK data over the full range of cyclic crack growth behavior tend to follow the typical sigmoidal shape shown in Figure 1. However, in the presence of an aggressive environment, the shape and location of da/dN -versus- ΔK curves can vary widely as a function of numerous parameters including (i) alloy composition, microstructure and strength level, (ii) cyclic frequency and waveform, (iii) electrochemical potential of the specimen, and (iv) crack size, in the case of very small cracks.

Figure 2 illustrates the most commonly used basis for describing stress-corrosion crack growth. Time-based crack growth rates (da/dt) are plotted versus the Mode I crack-tip stress-intensity factor (K_I) on log-log coordinates. As in the previous example, the curves tend to follow a sigmoidal shape, often with a distinct plateau in the mid-region.

Both types of crack growth curves are bounded by fracture instability at the upper limit and by apparent thresholds, below which crack growth does not occur, at the lower limit. The fatigue threshold parameter is termed ΔK_{th} and the stress-corrosion threshold parameter is termed K_{ISCC} . Herein lies one important area of distinction between these two types of environmental cracking, i. e., the importance of threshold behavior and its measurement.

In fracture-mechanics-based stress-corrosion methodology, a great deal of emphasis is placed on prevention; i. e., developing and/or selecting materials which exhibit high K_{ISCC} values. For the broad range of structural alloys, K_{ISCC} values can vary from near 10 to over 100 $\text{ksi}\sqrt{\text{in.}}$. In many applications, stress-corrosion cracking can be prevented by judicious material selection and/or effective environmental protection. Unlike metal fatigue, relatively little engineering guidance exists in the form of established codes and standards for sustaining stress-corrosion cracking damage over long periods of time without failure. Thus, although the portions of the da/dt -versus- K_I curve which lie above the K_{ISCC} threshold tend to be of scientific and engineering interest, special emphasis is placed on the measurement and use of the K_{ISCC} parameter.

In fatigue, ΔK_{th} values tend to be confined to a range of about 1 to 10 $\text{ksi}\sqrt{\text{in.}}$, meaning that the stress level/flaw size conditions for

nonpropagating cracks are restricted to low stresses and small crack sizes. Thus, the role of prevention in corrosion-fatigue crack growth is necessarily more limited than is the case for stress-corrosion cracking. With corrosion fatigue, greater practical interest is placed on the kinetics of growing cracks and on how the crack growth process is influenced by environmental factors.

Several important generalizations about aqueous environmental cracking apply to both phenomena: (i) sensitivity to cracking is very material dependent and environment dependent, thus enhancing the need for experimental characterization, (ii) cracking behavior can be strongly time-dependent, which can result in requirements for prolonged testing, (iii) cracking is caused by localized chemical action at crack tips, thus cracking behavior may bear little relationship to rising-load fracture toughness, (iv) sensitivity to cracking may be unrelated to other forms of environmental attack, thus alloys such as high-strength titanium that are resistant to general corrosion may still be highly prone to cracking, and (v) cathodic protection measures, which suppress general corrosion, may actually enhance those cracking mechanisms which are aided by hydrogen entry into the metal.

Finally, evidence exists to suggest that corrosion fatigue and stress-corrosion cracking can interact synergistically to produce cracking behavior that could not be predicted from considering either phenomenon separately. The condition which has been found to produce this effect is a small-amplitude cyclic stress superimposed on a much larger static stress, known as ripple loading. Ripple loading has been found to greatly increase the apparent propensity for cracking in some instances by a mechanism that remains to be identified.

Basic Mechanisms

The basic mechanisms of environmental cracking are complex and not fully understood. For stress-corrosion cracking, some of the proposed mechanisms are summarized in Table 1.⁷ These mechanisms can result in either transgranular or intergranular cracking. Part of the complexity surrounding mechanisms arises from the fact that, for a particular alloy/environment system, they can vary depending upon environmental factors such as the electrochemical potential of the specimen. However, from the standpoint of materials testing with precracked specimens, the same test methods are used regardless of the cracking mechanism involved.

What is important from a testing standpoint is that test methods be developed and standardized which neither accentuate nor suppress the operative cracking mechanisms being characterized, and that reproducible results be obtainable. But, given our present state of knowledge of environmentally-induced reactions at crack tips, it is not always obvious how to achieve this result. For instance, the role of solution aeration in promoting or inhibiting environmental cracking is not well defined. Opinions may abound, but definitive models and supportive data simply do not exist. Similar questions regarding the comparability of data obtained using an impressed current device versus using sacrificial anodes remain unresolved. Also, for cracking involving marine environments, it is not clear as whether reactions in natural sea water, such as biofouling and calcareous deposits, play an important role or whether laboratory substitute solutions produce equivalent results.

Test Method Development

Within ASTM Committee E-24, test method development is proceeding on standards for both corrosion-fatigue crack growth and stress-corrosion cracking in cooperation with Committees E-09 and G-01. This work is being conducted by Task Group E24.04.02 on Environmental Cracking. This task group is newly organized and represents a merger of previously separate task group activities within Committee E-24 on corrosion-fatigue crack growth and stress-corrosion cracking.

Recently, balloting has been conducted on revision of E 647 - 83, Standard Test Method for Constant-Load-Amplitude Fatigue Crack Growth Rates Above 10^{-8} m/Cycle. The proposed revisions to E 647 include an Annex on Special Requirements for Testing in Aqueous Environments. This proposed annex includes provisions for recommended apparatus and procedures to be used in conducting tests with several types of standard fracture mechanics specimens in aqueous environments at temperatures and pressures at, or near, ambient.

In the area of stress-corrosion cracking, activity within Committee E-24 is focused on developing a draft standard test method for measurement of the K_{ISCC} threshold parameter. This current work is building upon a long-time effort in this direction which included a successful interlaboratory program to evaluate fracture mechanics procedures for K_{ISCC} measurement, described by Wei and Novak in ASTM STP 821.⁴ Numerous problems remain to be resolved in developing a satisfactory K_{ISCC} standard test method. However,

progress in this area is evolving and a draft test method document is anticipated in the near future. It should also be noted that the International Organization of Standardization has drafted a standard on "Recommendations for Machining and Using Precracked Specimens."

Standards development in both of these areas of materials testing has benefited greatly from recent efforts by Navy laboratories to conduct studies leading to the development of Navy standard test methods for corrosion-fatigue crack growth and stress-corrosion cracking in marine environments. Navy laboratories have been conducting comprehensive studies on the influence of experimental parameters on environmental cracking test results for several years. This work has assisted in furthering the development of ASTM standards.

Interpretation and Utilization

Methodology for interpretation and utilization of standard test method data for environmental cracking is not well developed. This type of materials characterization data tends to be used on an ad hoc basis in most instances. One notable exception is the evolving methodology for inservice inspection of nuclear reactor coolant systems being developed by the American Society of Mechanical Engineers.⁸ This methodology is being developed for the prediction of flaw growth in several ferritic steels under cyclic loading in the presence of a high-temperature high-pressure aqueous environment. In the case of stress-corrosion cracking, the K_{ISCC} parameter is utilized in materials development and materials selection for high-strength alloys used in marine and aerospace applications. However, if past experience with other standard fracture mechanics tests is a guide, the development of standards for environmental cracking will serve to promote the development of engineering methodology and the use of data base information.

Future Developments

Once existing standards development tasks are completed, additional questions remain to be addressed. Several of these are as follows.

(1) How to deal with long-term environmental cracking? Many of the critical issues in this area involve the service life of materials over many years, decades, or even centuries. This focuses testing efforts on the measurement of threshold conditions. In many instances, true threshold

conditions cannot be reached in the time periods normally allotted to materials testing programs. Current test methods now under consideration tend to measure acceptably low crack growth rates rather than true thresholds. Also, very long-term materials testing involving aqueous environments involves numerous experimental complications, due to various corrosive reactions on test specimens and experimental apparatus as well as the long-term electronic stability of instrumentation.

(2) How to develop test methods which accurately reflect the potential interaction of corrosion-fatigue crack growth and stress-corrosion cracking? In many instances, actual service conditions involve both static and cyclic loading. Such interaction is not reflected in current standard test method development. For purposes of test method development, the two phenomena are now treated separately. To the extent that under some conditions the two phenomena can interact synergistically, existing approaches to standard test method development may produce nonconservative data in some instances.

(3) Can standard accelerated test methods be developed? The time now required in conducting environmental cracking tests is an impediment to the development of data. Clearly, a need exists for accelerated test methods, provided that such tests can produce valid results which can be interpreted for application to long-term cracking problems. Efforts in this direction have been undertaken in the past, primarily using accelerating environments such as hydrogen sulfide or high chloride concentrations. More recently, slow-strain-rate rising-load tests have been investigated. This topic is a matter of prime importance in regard to ASTM standards development.

Bibliography

¹J. A. Bennett and Harold Mindlin, "Metallurgical Aspects of the Failure of the Point Pleasant Bridge," Journal of Testing and Evaluation, March 1973, pp. 152-161

²Corrosion Fatigue (Proceedings of the First USSR-UK Seminar on Corrosion Fatigue of Metals, Lvov, USSR, 19-22 May 1980), R. N. Parkins and Ya. M. Kolotyarkin, Eds., The Metals Society, London, 1983

³Corrosion Fatigue: Mechanics, Metallurgy, Electrochemistry, and Engineering (Proceedings of the ASTM/Metal Properties Council Symposium on Corrosion Fatigue: Mechanics, Metallurgy, Electrochemistry and Engineering, St. Louis, MO, 21-22 October 1981), ASTM STP 801, T. W. Crooker and B. N. Leis, Eds., American Society for Testing and Materials, 1983

⁴Environment-Sensitive Fracture: Evaluation and Comparison of Test Methods (Proceedings of the ASTM/ National Bureau of Standards Symposium on Environment-Sensitive Fracture: Evaluation and Comparison of Test Methods, Gaithersburg, MD, 26-28 April 1982), ASTM STP 821, S. W. Dean, E. N. Pugh and G. M. Ugiansky, Eds., American Society for Testing and Materials, 1984

⁵Embrittlement by the Localized Crack Environment, (Proceedings of the TMS-AIME/MSD-ASM Symposium on Localized Crack Chemistry and Mechanics in Environment-Assisted Cracking, Philadelphia, PA, 4-5 October 1983), R. P. Gangloff, Ed., The Metallurgical Society of AIME, Warrendale, PA, 1984

⁶"Characterization of Environmentally Assisted Cracking for Design: State of the Art," National Materials Advisory Board, Publication NMAB-386, National Academy Press, Washington, DC, 1982

⁷A. J. Sedriks, Corrosion of Stainless Steels, Wiley-Interscience, New York, NY, 1979, p. 141

⁸ASME Boiler and Pressure Vessel Code, Section XI, Rules for Inservice Inspection of Nuclear Reactor Coolant Systems, American Society of Mechanical Engineers, 1980

Table 1

Suggested Classification of Stress-Corrosion Cracking Mechanisms⁷

Dissolution Mechanisms

Film Rupture Crack propagation occurs by local dissolution of metal at the crack tip due to prevention of passivation owing to plastic deformation.

Stress Accelerated Dissolution Crack propagation occurs by localized anodic dissolution. The principal role of plastic deformation is to accelerate the dissolution process.

Mechanical Mechanisms

Hydrogen Embrittlement Hydrogen accumulates within the metal in the crack-tip region, leading to localized weakening either by void formation or lowering of cohesive strength. Crack propagation occurs by mechanical fracture of the weakened region.

Adsorption Surface-active species adsorb and interact with strained bonds at the crack tip, causing a reduction in bond strength leading to crack propagation.

Mixed Mechanisms

Brittle Film Crack propagation occurs by repeated formation and rupture of a brittle film which grows into the metal at the crack tip.

Tunnel Mode Crack propagation occurs by formation of deep pits or tunnels via dissolution, followed by linking of these pits or tunnels by ductile rupture.

LOG CRACK GROWTH RATE, da/dN

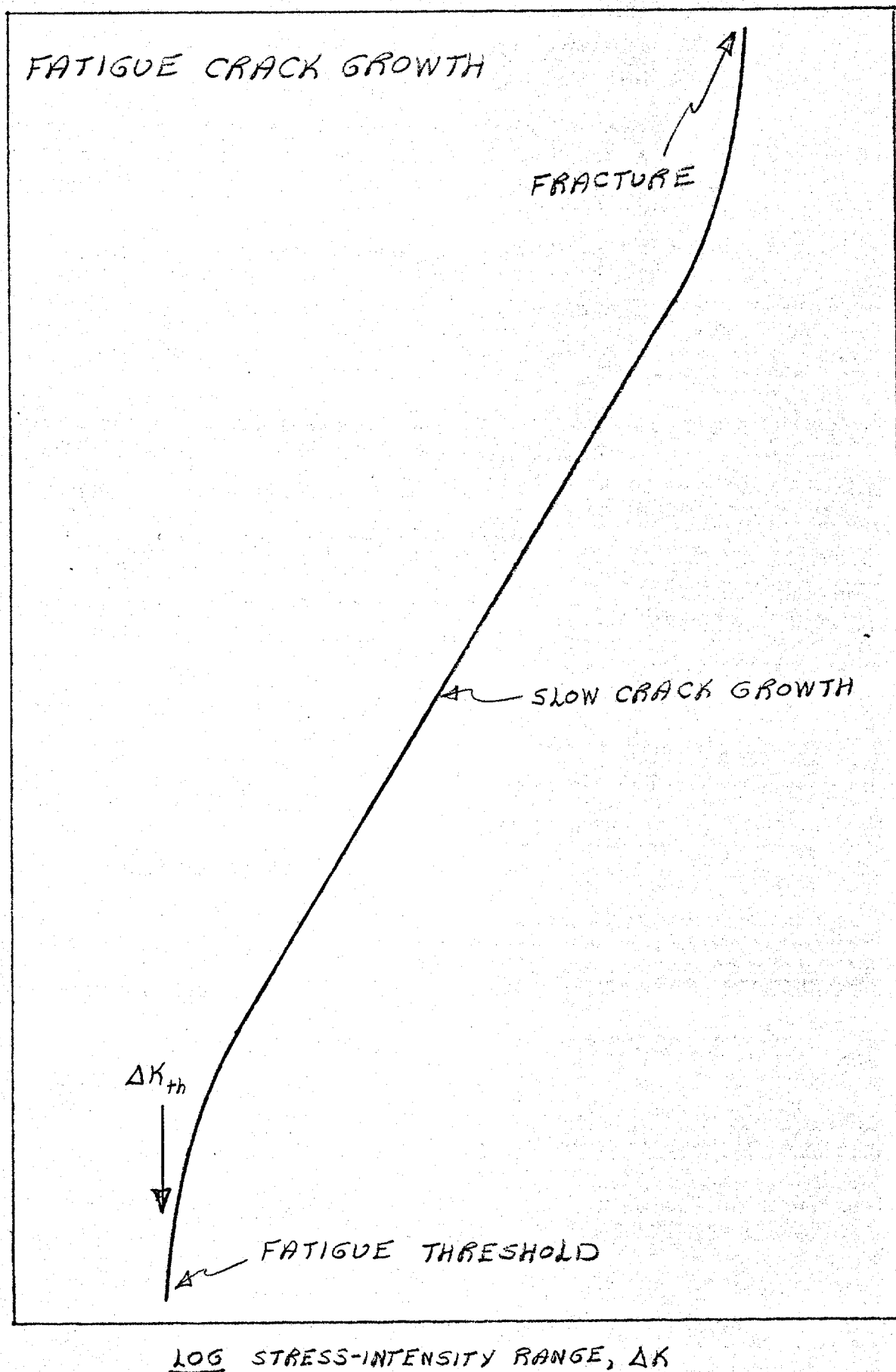
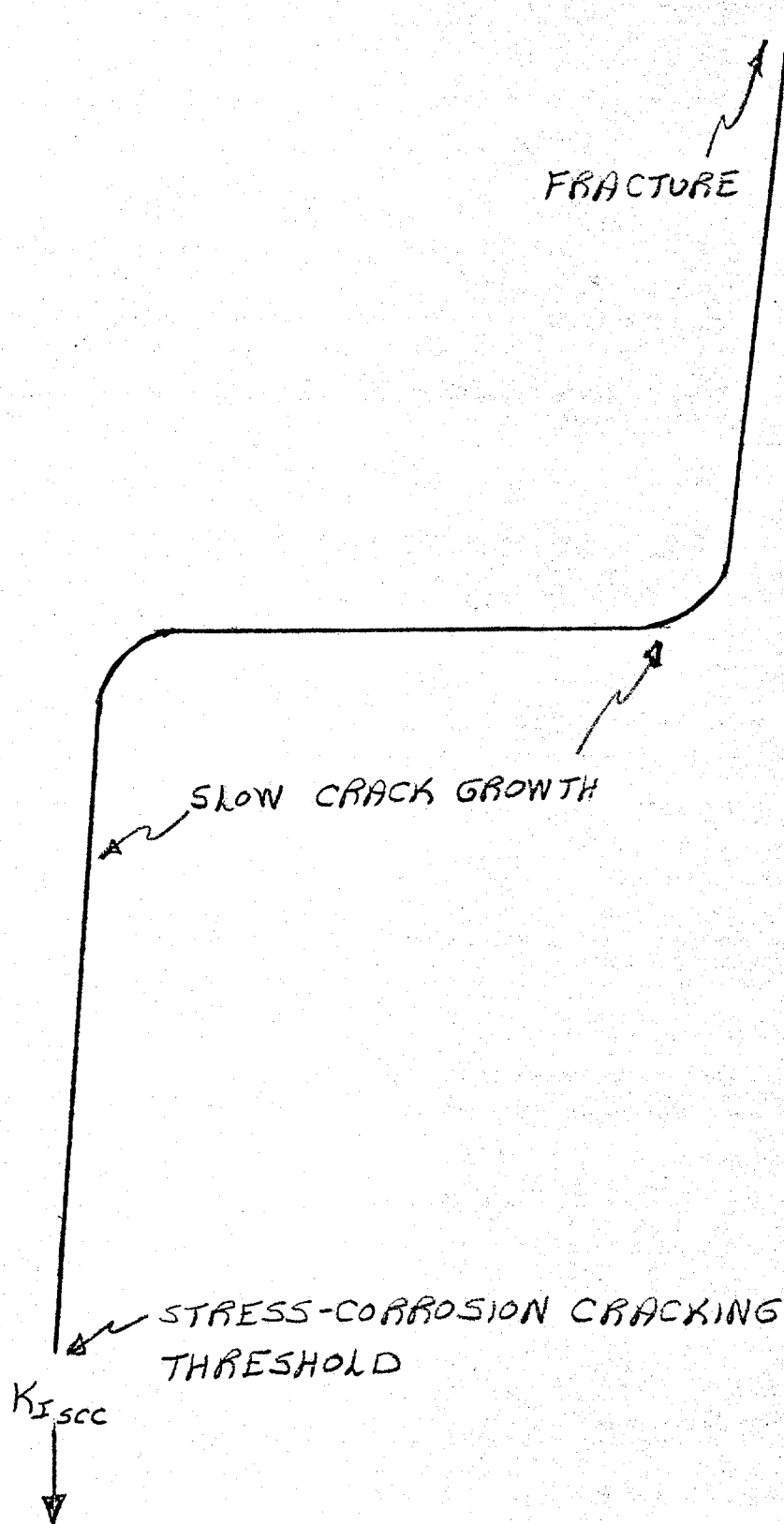


Figure 1

LOG CRACK GROWTH RATE, da/dt

STRESS-CORROSION CRACKING



LOG STRESS-INTENSITY, K_I

Figure 2